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Effect of the sequence of potassium introduction to V_2O_5/TiO_2 catalysts on their physicochemical properties and catalytic performance in oxidative dehydrogenation of propane

Dominique Courcot [a], Anne Ponchel [b], Barbara Grzybowska [b,1], Yolande Barbaux [c], Monique Rigole [b], Michel Guelton [b], J.P. Bonnelle [b]

[a] *Laboratoire de Catalyse et Environnement, Université du Littoral, 17, Avenue Blériot, 62 100 Calais, Cédex, France*
[b] *Laboratoire de Catalyse Hétérogène et Homogène, URA CNRS 402, Université des Sciences et Technologies de Lille, 59 655 Villeneuve d'Ascq, Cédex, France*
[c] *Université d'Artois, Faculté des Sciences Jean Perrin, SP 18, 62 307 Lens, Cédex, France*

Abstract

Two series of K-promoted V_2O_5/TiO_2 catalysts were prepared by: (a) deposition of vanadia on K-doped TiO_2 support (TiK V preparations), and (b) deposition of K on vanadia–titania catalysts (TiV K preparation). They were characterized by ^{51}V NMR, XPS, surface potential (work function) techniques and isopropanol decomposition, a probe reaction for the acid–base properties, and tested in oxidative dehydrogenation of propane (ODH). It has been found that the sequence of the K introduction in the preparation step is preserved in the calcined preparations, with more potassium being present on the surface of TiV K than TiK V catalysts. The vanadium species on TiK V samples include V_2O_5 and polymeric $[VO_x]_n$ species. The TiV K sequence leads to the formation of potassium vanadates (KV_3O_8 and possibly KVO_3), and to the decrease in the amount of V_2O_5. The TiV K catalysts are more active and selective in the ODH of propane, and more active in isopropanol dehydrogenation to the acetone (thus more basic) than the TiK V samples.

Keywords: Propane oxidative dehydrogenation; K-doped V_2O_5/TiO_2 catalysts

1. Introduction

The effect of the presence of potassium in the V_2O_5/TiO_2 catalysts on their physicochemical properties and catalytic performance in selective oxidation reactions has recently been a subject of several papers [1–7]. The interest in the problem has arisen from the fact that on one hand potassium is a common promoter in oxide catalysts and on the other hand it is often present as an impurity in most of commercial titanias. As shown in papers up to now, the potassium additive may exert a positive or detrimental effect on the yield and selectivity of the partial oxidation products, depending on the K/V ratio, the type of the oxidized molecule and the reactions conditions.

In the case of oxidative dehydrogenation (ODH) of propane, a reaction of great interest as a route to cheap propene, the addition of

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[1] On leave from Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland.

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small amounts of potassium to V_2O_5/TiO_2 catalysts ($K/V = 0.1$) led to the decrease in total activity, and the increase in the yield and the selectivity to propene [5,7]. The maximum yield obtained, ~ 10%, was not much lower than those reported so far for the best catalysts for this reaction, V–Mg–O [8–10] and Ni MoO4 [11] (13–15%). This justified further more detailed studies.

In the previous work, potassium was introduced after [5] or simultaneously [7] with the deposition of the vanadia phase on the titania support. A recent study [12], in which different amounts of vanadia were introduced on TiO_2 doped with controlled amounts of potassium, showed that the highest yields of propene and selectivity in propane ODH are observed for catalysts containing 1–2 theoretical monolayers (mnl) of vanadia (1 mnl $V_2O_5 \sim 10\ V \cdot nm^{-2}$ [13]), deposited on TiO_2 precovered by 1 mnl of potassium. The latter has been estimated earlier as equivalent to $2.5\ K \cdot nm^{-2}$ [14].

It then seemed of interest to study the effect of the sequence of K introduction to the V_2O_5/TiO_2 catalysts on their physicochemical and catalytic properties.

In the present work catalysts containing the same nominal amounts of vanadium and of potassium were prepared either by deposition of a vanadia phase on K-doped titania, or by adding potassium after deposition of vanadia on pure titania. They were characterized by ^{51}V NMR, XPS and surface potential SP (work function) techniques, and they were tested for ODH of propane and for the isopropanol decomposition — a probe of acid–base properties [15,16].

2. Experimental

2.1. Catalysts

The titania support was a commercial product of Tioxide Ltd. of specific surface area 27 $m^2 \cdot g^{-1}$. The XRD analysis showed it to be pure anatase. No surface impurities were detected by the XPS analysis. Elementary analysis with the plasma torch (ICP.AES), however, showed the presence of Cr (12 ppm), Cu (160 ppm), and S (0,13%). The support was calcined before use for 4h at 700°C. After calcination its BET specific surface area slightly decreased to 23 $m^2 \cdot g^{-1}$ and no sulfur was detected.

Two types of samples, each one containing $2{,}5\ K \cdot nm^{-2}$ and 10 or 20 $V \cdot nm^{-2}$ were prepared. In the first type of preparation, denoted further in the text by symbols TiK 10V or TiK 20V, vanadium was introduced on TiO_2 surfaces doped previously with potassium. The doping was performed by impregnation from the $KHCO_3$ solution, evaporation and drying for 12h at 120°C followed by calcination for 4h at 500°C. Vanadia was then deposited on the support by the grafting method in anaerobic conditions, using vanadyl isopropoxide dissolved in toluene as a precursor. The appropriate amounts of the isopropoxide solution were introduced under continuous stirring to a vessel containing a suspension of the support in toluene and this mixture was stirred for 10 minutes. Toluene was then evaporated at 40°C and the remaining yellow powder was dried for 12h at 100°C and calcined in dry air for 4h at 400°C.

In the second type of samples, Ti10V K or Ti20V K, vanadia was first introduced in the way given above onto a pure TiO_2 surface, then potassium was deposited on the calcined V_2O_5/TiO_2 samples by the incipient wetness method from a $KHCO_3$ solution. The preparations were again dried and calcined in air for 4h at 400°C.

3. Techniques

3.1. NMR measurements

^{51}V MAS NMR spectra were recorded at 105.2 MHz on a Bruker ASX 400 spectrometer equipped with MAS probe for 4 mm o.d. rotors. Spinning speeds up to 15 kHz were used. In all experiments, a single pulse excitation was applied with a pulse width of 1 μs ($\pi/12$ flip angle) and a recycling time of 0.7 s. The isotropic chemical shifts were referred to external $VOCl_3$ and were not corrected for second-order quadrupolar induced shifts. V_2O_5 was used as a second external reference (δ iso = −609 ppm). The δ scale is positive towards lower shielding.

3.2. Surface potential

The surface potential was measured with the vibrating condenser method; the method and the experimental set-up have been described in (14). The measurements were performed under a flow of 20% O_2 in Ar in the temperature range 50–450°C. The values of the surface potential Φ reported in the text are relative to the graphite electrode, an increase in Φ indicating that the surface is becoming more negatively charged. The surface potential values were reproducible for a given sample within 5 mV.

3.3. XPS spectra

The XPS spectra of the samples were recorded with an AEI-ES 200B spectrometer. The atomic ratio of the elements on the surface, n_A/n_B, was calculated from the intensity ratio I_A/I_B with the formula: $I_A/I_B = \sigma_A/\sigma_B(E_A^{kin}/E_B^{kin})^{1.77}n_A/n_B$; values of σ being taken after Scofield [17].

3.4. Catalytic activity measurements

The activity of catalysts in oxidative dehydrogenation of propane was measured in a fixed bed flow apparatus at 350 and 400°C. The reaction mixture contained 5 vol% C_3H_8 and 15 vol% O_2 diluted in nitrogen. 1 ml of the samples was used in the experiments, the contact time being 1 s. Analysis of products and unreacted propane was performed by on-line chromatography.

Propene, carbon monoxide, and carbon dioxide were found to be the main reaction products. The amounts of C_2 hydrocarbons and the oxygenates (acrolein, acetaldehyde, acrylic and acetic acid) were below 1% of the total amount of products.

3.5. Decomposition of isopropanol

Decomposition of isopropanol (isoPrOH) to propene and acetone was studied at 170°C with the pulse method, using dried helium as a carrier gas. 0.1 g of the sample and 2 μl of isoPrOH were used and the total flow-rate of helium was 30 ml/min. Prior to the test, the samples were treated in a stream of dried helium for 2h at 250°C. Analysis of products was performed by gas chromatography. The conversion of isoPrOH decreased slightly with the successive pulses, due to formation of a carbon deposit, the propene yield per pulse decreasing faster than that of acetone. The amounts of products per pulse reported further in the text are the means of the values obtained in three successive pulses after the stationary state of the activity was attained. The pure and K-doped titania support were practically inactive in the reaction.

4. Results and discussion

4.1. NMR measurements

The ^{51}V MAS NMR spectra of Ti10V, TiK 10V and Ti10V K are shown in Fig. 1. Table 1 summarizes the NMR data obtained. The shape of the sideband pattern associated with the isotropic peak at −609 ppm on the Ti10V and TiK 10V samples is characteristic of V_2O_5 [18,19]. It should be noted that on these two samples, V_2O_5-like species are largely predominant. Examination of the NMR spectrum of Ti10V K also shows a sideband pattern with an envelope nearly the same as that for V_2O_5 but, in this case, the isotropic peak is slightly shifted towards lowfield (δiso = −606 ppm). The V_2O_5-like species do not seem to be the major

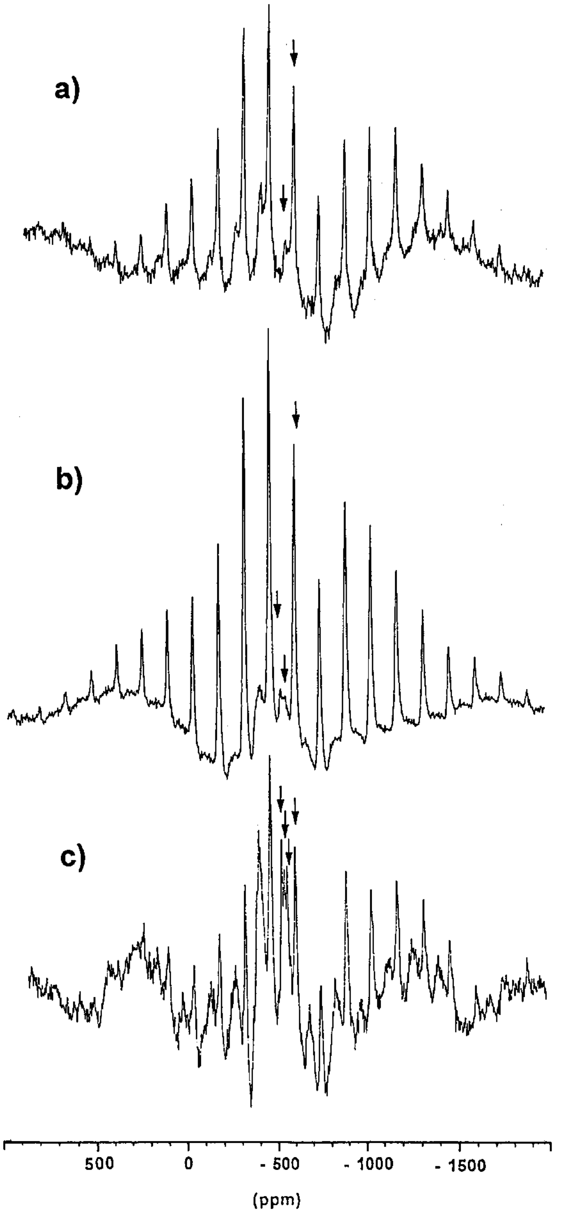

Fig. 1. ^{51}V MAS NMR spectra of Ti10V (a), TiK 10V (b), and Ti10V K (c) samples. Isotropic chemical shifts are indicated by arrows.

ones for this catalyst. In addition to V_2O_5 species, the spectrum of Ti10V exhibits a weak sideband pattern with an isotropic peak at −560 ppm (species II). The sideband envelope appears similar to the sideband feature of V_2O_5, mainly given by the chemical shift anisotropy (CSA). The same signal has been observed previously for V_2O_5/TiO_2 catalysts at submonolayer vanadia content [12], and has been ascribed to polymeric vanadates detected on this system by the Raman spectroscopy [20]. Species II seem also to be present in the TiK 10V sample, but in this case the sideband pattern is not well resolved.

The NMR spectrum of Ti10V K is more complex than the first two spectra. Beside V_2O_5 (δiso = −606 ppm) and species II (δiso = −559 ppm), four other signals can be detected at δiso = −505, −528, −541 and −548 ppm. The overlapping of the sidebands associated with these different isotropic peaks does not allow an evaluation of their chemical shift anisotropy. The relatively intense peak at −528 ppm with few sidebands has been attributed in a previous study [12] to tetrahedral species (III). Such species are also present in the TiK 10V samples, but in very small quantity.

Higher numbers of sidebands seem to be associated with the peaks at −541 and −548 ppm thus indicating that the CSA of these two species is greater than that of species III, and consequently the environment of vanadium is more distorted. According to the literature data [21] a peak at −548 ppm associated with the small one at −505 ppm can be assigned to the vanadate KV_3O_8, which contains two non-equivalent vanadium atoms in square-pyramidal environment. In the preceding study [12], potassium metavanadate KVO_3 was observed in V_2O_5/TiO_2 catalysts at low vanadium content with ^{51}V NMR. In this study the presence of KVO_3 cannot be ruled out since its isotropic peak at −552 ppm is very close to −548 ppm [12,21]. The presence of a small peak at −505 ppm, however, favours the presence of KV_3O_8. It is important to note that neither of the potassium vanadates was detected in the TiK 10V sample. The order of the potassium introduction then appears to affect the type of vanadium containing species. In the case of the Ti10V K sample, one cannot exclude the possibility that some part of the vanadia phase deposited on TiO_2 dissolved in the $KHCO_3$ solution during the

Table 1
^{51}V MAS NMR analysis: isotropic shift values (δiso) for vanadium species of different samples

Sample	V_2O_5 ppm	(II) ppm	(III) ppm	KV_3O_8 V(1) ppm	KV_3O_8 V(2) ppm
Ti10V	−609	−560	/	/	/
TiK 10V	−609	−560	−532	/	/
Ti10V K	−606	−541/−559	−528	−548	−505

preparation, to form the vanadates in the liquid phase. For the TiK 10V sample in which vanadium is introduced in nonaqueous medium on the K-doped titania, the vanadates can be formed only by the solid state reactions which require higher temperatures. The assignment of the peak at about −541 ppm cannot be made at present, no such signal being reported in the literature on vanadium compounds. It could be suggested that it corresponds to other types of polymeric $[V-O-V]_n$ species II, modified by interaction with potassium. In fact, in the previous work [12] a peak at −546 ppm was observed at lower vanadium and potassium content and ascribed to such a species: the shift from −560 ppm (species II) to −546 ppm was explained by the decrease in the electron density around vanadium atoms, resulting in a downfield shift in the NMR spectrum. Summing up the NMR data obtained in this work we may state that V_2O_5 and vanadia polymeric species are present in all of the samples studied. Additionally potassium vanadates appear for the catalyst in which potassium was introduced after the vanadia phase had been deposited on TiO_2. Much less vanadia relative to other species is observed for this catalyst.

4.2. XPS data

Table 2 gives the values of binding energies, BE for O1s, V2p3/2 and K2p3/2 levels, and the surface atomic ratio of different elements in the studied catalysts. The BE of V2p3/2 varies between 517.1 and 517.5 eV, the values reported for V^{5+} ions. Though the variations are higher than the usual uncertainty in the BE values (0.2 eV) no definite trend with the vanadium content or the order of K introduction is observed. In addition no marked difference in BE of V2p3/2 level for the undoped and K-doped samples is observed. The BE's of the K2p3/2 level are, on the other hand, higher for the TiV K catalysts as compared with the TiK V samples, which implies lower electron density (more cationic character) around potassium atoms for the former samples. The difference in the degree of potassium cationization can be due to different potassium environments in the two groups of catalysts, Ti–O–K bonds being present in the TiK V series and V–O–K bonds being present in the TiV K series. Higher electronegativity, E.N. of vanadium (1.63) as compared with that of titanium (E.N. 1.54) would lead to more extensive withdrawal of electrons

Table 2
Binding energy, BE for O1s, V2p3/2 and K2p3/2 levels and surface atomic ratio of different elements in catalysts

Sample	Binding energy (eV)			Surface atomic ratio	
	O1s	V2p3/2	K2p3/2	V/Ti	K/V
Ti10V	530.2	517.0	/	0.151	/
Ti20V	530.2	517.1	/	0.157	/
TiK 10V	530.0	517.1	293.4	0.161	0.30
TiK 20V	530.4	517.5	293.2	0.176	0.25
Ti10V K	530.2	517.2	293.7	0.148	0.36
Ti20V K	530.3	517.2	293.6	0.159	0.28

from potassium in the case of the Ti VK samples. It should, however, be observed that the BE values of potassium for the preparations studied in this work are higher than those of the potassium vanadates: BE = 292.6 ± 0.1 eV has been registered for K2p3/2 level in KVO_3 and KV_3O_8, prepared separately as reference compounds. Thus, though the NMR data show the presence of potassium vanadates, their quantity is either too low to affect the XPS signal of K, or they are not present in the upper surface layers of the catalysts. As suggested previously [12,14] potassium atoms can be located over oxygen atoms in vanadia (V_2O_5 or polymeric) species or over TiO_2, replacing surface protons and giving rise to V–O–K and Ti–O–K surface bonds of different types than those in the bulk compounds.

The surface atomic ratio V/Ti changes only slightly with the sequence of the K deposition and does not differ much for the K-doped and undoped catalysts. Slightly higher V/Ti ratios are observed for TiK V as compared to TiV K preparations. The very small differences in the V/Ti values for Ti10V and Ti20V samples are in agreement with the previous XPS data on undoped V_2O_5/TiO_2 catalysts; showing a practically constant value of this ratio at V content exceeding the monolayer coverage. This was explained by the formation of V_2O_5 'towers' at high vanadium content covering the bidimensional monolayer structure of dispersed vanadia [22,23].

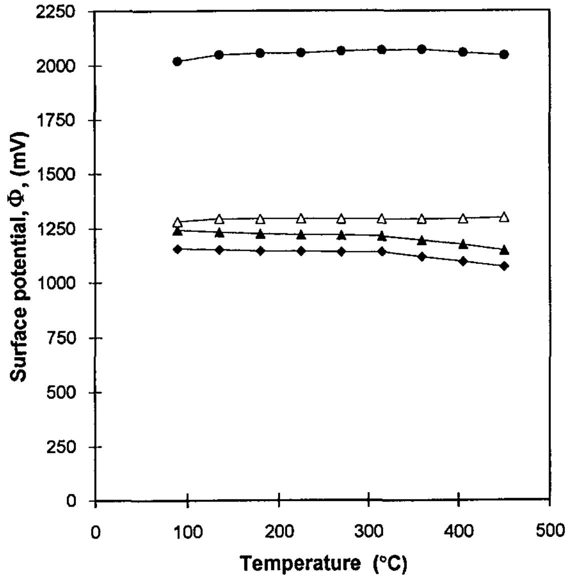

Fig. 2. Changes in surface potential Φ with the temperature in the O_2/Ar mixture for catalysts: – • – Ti10V; -▲- TiK 10V; – ◆ – Ti10V K and -△- TiK 20V.

The K/V ratio is higher for the TiV K as compared with TiK V catalysts, especially at lower vanadium content. The order of the K introduction during the catalyst preparation seems then to be preserved in the calcined solids. Potassium on the TiO_2 surface does not, however, appear completely covered by the vanadia phase in the TiK V samples, the K/V ratios being quite high in this case.

4.3. Surface potential

Fig. 2 presents the changes in the surface potential, Φ with temperature in the O_2/Ar mixture for the TiK 10V, TiK 20V and Ti10V K samples and compares them with those for the undoped sample Ti10V.

The Φ values for K-containing preparations are much lower than those for the undoped catalysts indicating the lower negative charge of the K-doped surface. The small difference can, however, be observed for the samples with different sequences of K introduction, the Φ values for Ti10V K being lower than those of TiK 10V. The lowering of the surface potential on deposition of potassium on the oxide surface has been explained by the change of sign of the surface dipoles in the topmost surface layer of the solid [14], with potassium ions K^+ covering the negatively charged oxygen anions. The polarized surface metal–oxygen (Me–O) groups with oxygen ions sticking out of the surface give rise to the surface negative charge, whereas those with the exposed cations, give rise to the positive charge. The total value of the Φ depends on the relative amounts of the two types of surface dipoles $^{(\delta-)}O\text{–}Me^{n+}$ and $^{(\delta+)}Me^{n+}$–

O. The lower value of Φ for the Ti10V K as compared with TiK 10V preparation indicates thus, that more potassium is present in the top layer, covering oxygens of the surface V–O groups. In the TiK 10V sample, V–O groups partly covering potassium on the TiO_2 surface, with oxygen atoms oriented towards exterior of the solid, give rise to higher negative charge and hence higher Φ. It should, however, be observed that in the latter case, some part of the K-doped TiO_2 surface not covered with vanadia phase is exposed, the Φ values of the TiK 10V sample being much lower than those for the undoped Ti10V. Higher surface potential of the TiK 20V sample suggests that the excess of vanadia better covers the potassium atoms on the TiO_2 support, although not completely.

The surface potential measurements confirm then the XPS results showing that the sequence of K introduction in the preparation of the catalysts precursors is preserved in the calcined catalysts.

4.4. Isopropanol decomposition

Table 3 gives the amounts of propene and acetone formed in isopropanol decomposition on the catalysts used in this study. As seen, the main reaction in all cases is isopropanol dehydrogenation to acetone, the amounts of this product varying for different catalysts. For both (10 and 20 $V \cdot nm^{-2}$) vanadium amounts, higher amounts of acetone are formed on the VK samples as compared with KV. This can be due to the presence of higher amounts of the polymeric V–O–V species and potassium vanadates as well as to lower content of V_2O_5 in the VK as compared with the KV preparations, as indicated by the NMR data. In fact, the previous studies have shown that the dehydrogenation properties of the V_2O_5/TiO_2 catalysts are mainly due to the monolayer type species, with crystalline V_2O_5 being relatively inactive in the isopropanol dehydrogenation to acetone [16]. Potassium vanadates are also active in isopropanol dehydrogenation to acetone [24].

Table 3
Isopropanol decomposition on K-doped and undoped catalysts

Sample	10^6 mol·m^{-2}·s^{-1}	
	Propene	Acetone
TiK 10V	0.04	1.08
TiK 20V	0.05	0.86
Ti10V K	0.04	2.00
Ti20V K	0.07	1.31
Ti10V	0.13	0.96

Higher amounts of acetone on 10V than on 20V samples, irrespectively of the sequence of the K introduction, can be due to different reasons. On one hand one may argue that polymeric species are better exposed on the surface of catalyst with lower vanadium amounts, whereas they may be covered by an excess of an inactive form of vanadia once the monolayer coverage is exceeded. On the other hand, potassium vanadates also contribute to the acetone formation. Their relative content should be higher for the samples with higher K/V ratios (10V), which could also account for the difference in the acetone formation on the 10V and 20V catalysts.

The amounts of propene-a product of isopropanol dehydration-which can be taken as a measure of the catalyst acidity [15], are low and no definite trend can be observed for preparations with the different sequences of the potassium deposition. Higher amounts of propene are detected, however, for the non-doped Ti10V sample, indicating higher acidity of this catalyst. The decrease in acidity in the presence of potassium in V_2O_5/TiO_2 catalysts has been previously observed and ascribed to the replacement of protons, present on the non-doped sample, by potassium ions [5,7].

4.5. Catalytic activity

Table 4 gives the catalytic data in the ODH of propane at 350°C and 400°C for the catalysts studied. In agreement with the earlier work [5,7,12] a decrease in the propane conversion, $C \cdot C_3H_8$ and in the CO/CO_2 ratio and an

Table 4
Oxidative dehydrogenation (ODH) of propane at 350°C and 400°C of samples under study (5% C_3H_8, 15% O_2 in N_2, $\tau = 1$ sec)

Sample	Temperature (°C)	C. C_3H_8 (%)	S. C_3H_6 (%)	S. CO_x (%)	CO/CO_2
Ti10V	350	68.4	1.4	98.5	2.6
	400	77.3	0.7	99.1	2.5
	300 [a]	5.5	33.7	65.3	1.8
	350 [a]	18.2	17.6	82.4	2.0
TiK 10V	350	3.6	35.0	64.7	0.70
	400	12.6	22.6	78.2	0.73
TiK 20V	350	3.9	44.0	56.0	0.67
	400	13.6	25.1	74.0	0.67
Ti10V K	350	4.9	39.5	60.5	0.78
	400	17.4	22.2	78.0	0.78
Ti20V K	350	6.3	39.5	60.5	0.85
	400	18.7	21.3	78.7	0.91

[a] Contact time, $\tau = 0.2$ s.

increase in the selectivity to propene, $S \cdot C_3H_6$ can be observed for the K-promoted catalysts as compared with non-promoted Ti10V. It can be noted that the selectivities to propene for the K-doped samples are lower than the selectivities obtained at comparable conversions in the previous works [5,7]. The difference in the selectivity to propene at low propane conversions between the doped and non-doped samples in the present study is then smaller than in [5] and [7]. This can be due to the different methods of the catalyst preparation (grafting from vanadium isopropoxide in the present work, impregnation from NH_4VO_3 in [5] and [7]), and to different potassium precursor ($KHCO_3$ in the present work, KOH in [5], KNO_3 in [7]).

The sequence of the potassium introduction, however, affects the activity and selectivity of the catalysts. For the two vanadium amounts, 10 and 20V, the TiV K preparations show higher conversions than the TiK V samples. The comparison of the selectivities of different catalysts is more difficult, since conversions for each catalyst are different. Propane ODH is a consecutive reaction in which selectivity to the intermediate product in the sequence of oxidation steps-i.e., to propene-decreases with increasing conversion, the comparison of selectivities should be made at isoconversion. Nevertheless, we can observe that for 10V catalysts the selectivity to propene for the 10V K preparation, is higher at 350°C or comparable at 400°C than selectivity of the K 10V preparation, even though the conversions for the former sample are higher. For the 20V samples, the VK sequence leads to more active but less selective catalysts as compared with KV samples.

The better performance of the VK catalysts as compared with KV catalysts can be explained by differences in the dispersion of the vanadia phase inferred from the NMR data. Higher proportions of V_2O_5 on KV samples could account for the lower activity and selectivity to propene of these catalysts. V_2O_5 formed in the V_2O_5/TiO_2 catalysts is known to be less active and less selective in the ODH of propane than the dispersed monolayer species [7]. It can be mentioned that Burch and Crabb [28] reported high selectivities to propene for pure V_2O_5. At high propane/air ratio and high reaction temperature (500°C) used in their study, V_2O_5, however, was reduced to lower vanadium oxides, which may have different catalytic properties than V_2O_5. Under the reaction conditions used in the present study (excess of air and reaction temperatures of 350 and 400°C), the reduction degree of the vanadia phase, verified by the chemical analysis was very low, the amount of vanadium ions of valency lower than $+5$ not exceeding 1–2% of total vanadium.

No straight forward explanation can be given for higher selectivities of TiK 20V catalyst as compared with the TiK 10V catalyst. Their activities (propane conversion) are very similar, which indicates that vanadia in excess of the monolayer coverage is practically inactive for propane oxidation, as it was found in the oxidation of other hydrocarbons, e.g. o-xylene on V_2O_5/TiO_2 system [25,26]. It may cover, however, the bare parts of the support, preventing overoxidation of propene to carbon oxides and thus leading to the increase in the selectivity. Different relative amounts of potassium vanadates with respect to the vanadia species in the 10V and 20V preparations could also account for the difference in the selectivity. Separate studies on the activity of potassium vanadates in propane ODH, now in course, should decide between these two explanations. It may be recalled at this point that potassium vanadate KV_3O_8 was found to be much less active and selective for partial oxidation of o-xylene than vanadium oxides or vanadates of higher vanadium content [27].

Formation of potassium vanadates can also partly account for the lower activity of K-containing samples in comparison with the undoped 10V catalyst. Since, however, polymeric V–O–V and V_2O_5 are the dominant vanadium species in this sample (as for the K-doped catalysts) the phase composition and type of dispersed species does not appear to be the only factor affecting catalyst activity. In fact the decrease in the acidity and increase in the basicity observed in previous works [5,7] and confirmed in this study for the K-doped samples, may explain their lower activity. The presence of K-atoms, replacing Brønsted acid centers reported on V_2O_5/TiO_2 catalysts, would eliminate nonselective route of oxidation on acidic centers [16], decreasing total activity.

5. Conclusions

The sequence of introduction of the potassium additive to V_2O_5/TiO_2 catalysts:

(a) K deposited first on the TiO_2 support and then vanadia added (TiK V preparations), or

(b) vanadia phase deposited on TiO_2 and then K added, (TiV K preparations), is preserved after the calcination of the catalysts precursors. The XPS and surface potential data indicate higher amounts of surface K on the TiV K catalysts than on the TiK V ones.

The different order of the introduction of potassium induces:

1. a different type of vanadium-containing species: as inferred from the NMR data in the TiK V catalysts, V_2O_5 and polymeric $[V\text{–}O\text{–}V]_n$ species are observed, whereas potassium vanadates KV_3O_8 were detected as additional species on the TiV K catalysts. The amount of V_2O_5 in these latter preparations is relatively low when compared to the amounts of the vanadates and polymeric species.
2. higher activity and selectivity to propene in the ODH of propane for the TiV K catalysts as compared with the TiK V ones. The TiV K samples are also more active for dehydrogenation of isopropanol to acetone which indicates higher basicity. The differences in the catalytic performance of the two types of catalysts can be ascribed to different distributions of the vanadium species, in particular, to the smaller amounts of the less active and non-selective V_2O_5 phase in the TiV K catalysts. It appears however that the type of vanadium containing species is not the single decisive factor to account for the modification of the catalytic performance of V_2O_5/TiO_2 catalysts in the presence of potassium. The modification of acid–base properties (decrease in the acidity and increase in the basicity for K doped samples) can also be important.

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